

## Structure of Bis(1,3-diphenyl-1,3-propanedionato)bis(tetrahydrofuran)manganese(II), an Unusual Product from the Reaction of (Methylcyclopentadienyl)tricarbonylmanganese with Bis(1,3-diphenyl-1,3-propanedionato)tin(II)

BY ANTHONY B. CORNWELL AND PHILIP G. HARRISON\*

Department of Chemistry, University of Nottingham, University Park, Nottingham NG7 2RD, England

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**Abstract.**  $C_{38}H_{38}MnO_6$ ,  $[Mn(C_4H_8O)_2(C_{15}H_{11}O_2)_2]$ ,  $M_r = 645.66$ , monoclinic,  $P2_1/c$ ,  $a = 9.923$  (5),  $b = 15.223$  (4),  $c = 10.832$  (5) Å,  $\beta = 103.42$  (8)°,  $V = 1592$  Å<sup>3</sup>,  $D_o = 1.38$ ,  $D_c = 1.35$  Mg m<sup>-3</sup>,  $Z = 2$ ,  $F(000) = 678$ ,  $\lambda(Mo K\alpha) = 0.71069$  Å,  $\mu(Mo K\alpha) = 0.486$  mm<sup>-1</sup>. Crystals are composed of discrete molecules of composition  $Mn(bppd)_2(H_4furan)_2$  in which the Mn atom enjoys almost perfect octahedral coordination by two chelating bppd groups and two  $H_4furan$  molecules [Mn—O(bppd) 2.088 (1), 2.136 (1) Å; Mn—O( $H_4furan$ ) 2.285 (2) Å;  $\angle OMnO$  84.76 (5)–95.24 (5)°].

**Introduction.** Irradiation of a mixture of (methylcyclopentadienyl)tricarbonylmanganese and bis(1,3-diphenyl-1,3-propanedionato)tin(II) in  $H_4furan$  yields the complex  $\{(MeC_5H_4)Mn(CO)_2[Sn(bppd)_2]\}$  as the initial product (Cornwell & Harrison, 1976). Following the separation of this amorphous product from the reaction mixture, the filtrate very slowly deposited claret-red crystals of a second product identified as the complex  $[Mn(bppd)_2(H_4furan)_2]$  [composition, found: C 70.87, H 5.82%;  $M_r = 690$  (osmometry in benzene);  $C_{38}H_{38}MnO_6$  requires: C 70.81, H 5.93%;  $M_r = 646$ ]. The cuboid crystals are air-sensitive, but stable to X-rays, and one of approximate dimensions  $0.4 \times 0.4 \times 0.5$  mm was mounted in a Lindemann capillary under nitrogen and used to obtain the initial cell parameters and also the subsequent intensity data. The space-group and initial cell parameters were obtained from oscillation, and zero- and first-layer Weissenberg photographs obtained using an equi-inclination Weissenberg camera. Relative intensities of reflections were collected up to  $\theta = 25.0^\circ$  using a Hilger & Watts Y290 four-circle diffractometer. All reflections with a corrected count of  $I < 3\sigma(I)$  were considered as non-observed and therefore not used, reducing the number of reflections used from 2380 to 2312. The intensities were corrected for Lorentz and polarization effects, but no absorption correction was made owing to the low  $\mu$  value. The structure was solved using Patterson and Fourier methods, and after the location of all the non-

hydrogen atoms, six cycles of full-matrix isotropic followed by four cycles of full-matrix anisotropic least-squares refinement resulted in convergence at an  $R$  value of 0.040. At this stage, an analysis of the mean  $\Delta F$  value for approximately equal intervals of  $F_o$  was carried out and the resulting weighting scheme  $w = 1/\{1.0 + [(F_o - B)/A]^2\}$  applied, where  $A = 15.00$  and  $B = 14.00$ . Two further cycles of full-matrix anisotropic least-squares refinement employing the weighting scheme reduced the  $R$  value to 0.037. Refinement was carried out using the *CRYSTALS* suite of programs. The scattering factors used were those for neutral atoms. The final fractional atomic coordinates are listed in Table 1.† The atomic numbering is illustrated in Fig.

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34155 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final fractional atomic coordinates

	x	y	z
Mn(1)	0.0000	0.5000	0.5000
O(1)	0.1710 (1)	0.4458 (1)	0.4461 (1)
O(2)	-0.0798 (1)	0.3691 (1)	0.4797 (1)
O(3)	0.1100 (2)	0.4775 (1)	0.7074 (2)
C(1)	0.2308 (3)	0.4241 (2)	0.7401 (3)
C(2)	0.1513 (3)	0.4553 (2)	0.9257 (2)
C(3)	0.2778 (3)	0.4255 (2)	0.8815 (3)
C(4)	0.0805 (3)	0.5146 (2)	0.8199 (3)
C(5)	-0.1436 (2)	0.2330 (1)	0.3811 (2)
C(6)	0.3036 (2)	0.3613 (1)	0.3375 (2)
C(7)	-0.2395 (2)	0.2177 (1)	0.4539 (2)
C(8)	0.4279 (2)	0.3976 (2)	0.4038 (2)
C(9)	-0.3417 (2)	0.1012 (2)	0.3151 (2)
C(10)	-0.2468 (2)	0.1155 (2)	0.2419 (2)
C(11)	-0.0446 (2)	0.3083 (1)	0.4149 (2)
C(12)	0.0797 (2)	0.3067 (1)	0.3729 (2)
C(13)	0.1776 (2)	0.3736 (1)	0.3895 (2)
C(14)	0.5413 (3)	0.3434 (2)	0.2473 (3)
C(15)	0.5466 (2)	0.3882 (2)	0.3582 (3)
C(16)	-0.1484 (2)	0.1806 (1)	0.2749 (2)
C(17)	0.2990 (2)	0.3166 (2)	0.2253 (2)
C(18)	0.4188 (3)	0.3079 (2)	0.1798 (2)
C(19)	-0.3373 (2)	0.1520 (2)	0.4216 (2)

\* To whom correspondence should be addressed.

1. Intramolecular bond distances and angles are listed in Table 2, and least-squares mean-planes data are collected in Table 3.

**Discussion.** The formation of Mn(bppd)<sub>2</sub>(H<sub>4</sub>furan)<sub>2</sub> in fair yield (31%) during the reaction of (methylcyclopentadienyl)tricarbonylmanganese and bis(1,3-diphenyl-1,3-propanedionato)tin(II) is unexpected since it involves (i) the cleavage of the methylcyclopentadienyl and carbonyl groups from manganese, (ii) the oxidation of manganese from Mn<sup>I</sup> to Mn<sup>II</sup> in the presence of the quite strongly reducing Sn<sup>II</sup>, and (iii) the transfer of both (bppd) ligands from tin to

manganese. At present we cannot account for the formation of this product, which is reproducible even when the concentrations of the reactants are varied. No similar products were obtained when other bis(1,3-ketoenolato)tin(II) compounds were used.

As may be seen from Figs. 1 and 2, the crystals of Mn(bppd)<sub>2</sub>(H<sub>4</sub>furan)<sub>2</sub> consist of discrete isolated molecules. The molecule is crystallographically centrosymmetric, and the two crystallographically equivalent H<sub>4</sub>furan and (bppd) groups give almost perfect octahedral geometry at manganese [ $\angle$ O(1)–Mn–O(2) 84.76 (5),  $\angle$ O(1)–Mn–O(3) 88.94 (6),  $\angle$ O(2)–Mn–O(3) 92.42 (7)<sup>o</sup>]. Octahedral or slightly distorted octahedral coordination at Mn<sup>II</sup> is quite common, and numerous compounds have been reported to possess this geometry. Diaquabis(2,4-pentanedionato)man-

Table 2. Intramolecular bond distances (Å) and angles (°)

Mn(1)–O(1)	2.088 (1)	C(5)–C(7)	1.389 (3)
Mn(1)–O(2)	2.136 (1)	C(7)–C(19)	1.381 (3)
Mn(1)–O(3)	2.285 (2)	C(9)–C(19)	1.381 (3)
O(1)–C(13)	1.267 (2)	C(9)–C(10)	1.381 (3)
O(2)–C(11)	1.261 (2)	C(10)–C(16)	1.379 (3)
O(3)–C(1)	1.424 (3)	C(5)–C(16)	1.392 (3)
O(3)–C(4)	1.434 (3)	C(6)–C(8)	1.389 (3)
C(1)–C(3)	1.493 (4)	C(8)–C(15)	1.387 (3)
C(3)–C(2)	1.513 (4)	C(14)–C(15)	1.372 (4)
C(2)–C(4)	1.499 (4)	C(8)–C(14)	1.375 (4)
C(12)–C(13)	1.391 (3)	C(17)–C(18)	1.395 (3)
C(6)–C(13)	1.498 (3)	C(6)–C(17)	1.384 (3)
C(11)–C(12)	1.410 (3)		
C(5)–C(11)	1.499 (3)		
O(1)–Mn(1)–O(2)	84.76 (5)	O(1)–Mn(1)–O(3)	88.94 (6)
O(2)–Mn(1)–O(3)	92.42 (7)	O(2)–Mn(1)–O(1)'	95.24 (5)
O(3)–Mn(1)–O(1)'	91.06 (6)	O(3)–Mn(1)–O(2)'	87.58 (7)
Mn(1)–O(1)–C(13)	127.94 (13)	Mn(1)–O(2)–C(11)	126.75 (13)
Mn(1)–O(3)–C(1)	120.90 (16)	Mn(1)–O(3)–C(4)	129.14 (15)
C(1)–O(3)–C(4)	109.9 (2)	O(3)–C(4)–C(2)	105.1 (2)
C(4)–C(2)–C(3)	102.4 (2)	C(2)–C(3)–C(1)	104.1 (2)
C(3)–C(1)–O(3)	107.0 (2)	O(1)–C(13)–C(12)	125.8 (2)
O(2)–C(11)–C(12)	124.7 (2)	C(13)–C(12)–C(11)	125.6 (2)
O(1)–C(13)–C(6)	115.6 (2)	O(2)–C(11)–C(5)	116.5 (2)
C(12)–C(11)–C(5)	118.8 (2)	C(12)–C(13)–C(6)	118.6 (2)
C(13)–C(6)–C(8)	118.3 (2)	C(13)–C(6)–C(17)	122.1 (2)
C(8)–C(6)–C(17)	119.6 (2)	C(6)–C(17)–C(18)	120.0 (2)
C(17)–C(18)–C(14)	119.7 (2)	C(18)–C(14)–C(15)	120.7 (2)
C(14)–C(15)–C(8)	120.0 (2)	C(15)–C(8)–C(6)	120.0 (2)
C(11)–C(5)–C(16)	122.3 (2)	C(11)–C(5)–C(7)	119.1 (2)
C(16)–C(5)–C(7)	118.5 (2)	C(5)–C(7)–C(19)	120.7 (2)
C(7)–C(19)–C(9)	120.1 (2)	C(19)–C(9)–C(10)	119.8 (2)
C(9)–C(10)–C(16)	120.0 (2)	C(10)–C(16)–C(5)	120.8 (2)

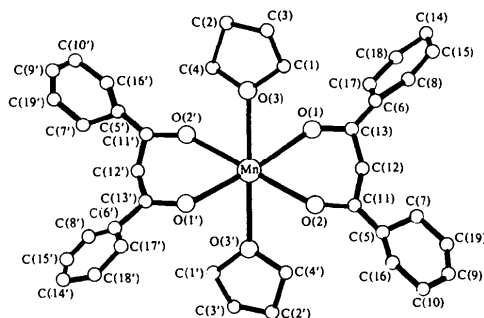


Fig. 1. View of the molecule of Mn(bppd)<sub>2</sub>(H<sub>4</sub>furan)<sub>2</sub>, showing the atomic numbering.

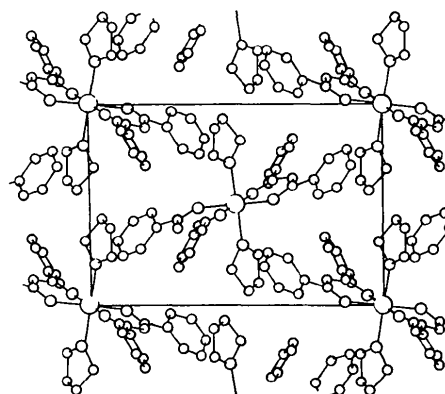


Fig. 2. Projection of the unit cell along [100].

Table 3. Equations of least-squares mean planes, deviations from the mean planes (Å), and angles between the planes

The e.s.d.'s for the deviations of atoms from the planes are  $\pm 0.001$  Å.

Plane 1: O(3), C(1), C(3), C(4), C(2)

$$5.6797x - 12.3980y - 0.4336z = 0.326$$

O(3) –0.070; C(1) –0.060; C(3) 0.163; C(2) –0.206; C(4) 0.173

Plane 2: O(1), C(13), C(12), C(11), O(2), Mn(1)

$$-3.3291x + 8.6020y - 7.0987z = -0.071$$

O(1) –0.170; C(13) 0.071; C(12) 0.203; C(11) 0.074; O(2) –0.107; Mn(1) –0.071

Plane 3: C(6), C(8), C(15), C(14), C(18), C(17)

$$-0.9793x + 12.9808y - 5.1568z = 2.656$$

C(6) –0.003; C(8) 0.003; C(15) 0.000; C(14) –0.004; C(18) 0.004; C(17) 0.000

Plane 4: C(5), C(7), C(19), C(9), C(10), C(16)

$$-5.0777x + 9.9257y - 4.6091z = 1.283$$

C(5) 0.003; C(7) 0.002; C(19) –0.005; C(9) 0.004; C(10) 0.001; C(16) –0.005

Angles between the planes (°)

(1)–(2)	136.39	(2)–(4)	15.88
(2)–(3)	25.63	(3)–(4)	26.69

Table 4. Comparison of Mn—O bond distances (Å) in Mn(bppd)<sub>2</sub>(H<sub>4</sub>furan)<sub>2</sub> with those of related complexes

Complex	r(Mn—O)
Mn(bppd) <sub>2</sub> (H <sub>4</sub> furan) <sub>2</sub>	to bppd: 2.088 (1), 2.136 (1) to (H <sub>4</sub> furan): 2.285 (2)
Mn(C <sub>5</sub> H <sub>7</sub> O <sub>2</sub> ) <sub>2</sub> ·2H <sub>2</sub> O <sup>(a)</sup>	to C <sub>5</sub> H <sub>7</sub> O <sub>2</sub> : 2.129 (7), 2.150 (8) to H <sub>2</sub> O: 2.267 (8)
Mn(CHO) <sub>2</sub> ·2H <sub>2</sub> O <sup>(b)</sup>	to CHO: 2.172 (12) to H <sub>2</sub> O: 2.216 (13), 2.168 (15)
Mn <sub>2</sub> (C <sub>3</sub> H <sub>8</sub> N) <sub>2</sub> (C <sub>5</sub> H <sub>7</sub> O <sub>2</sub> ) <sub>2</sub> <sup>(c)</sup> Mn <sup>2+</sup> (POCl <sub>2</sub> ) <sub>2</sub> (MeCO <sub>2</sub> Et) <sub>2</sub> <sup>(d)</sup>	to C <sub>5</sub> H <sub>7</sub> O <sub>2</sub> : 2.14 (2) to POCl <sub>2</sub> : 2.12, 2.14 to EtO <sub>2</sub> CMe: 2.17, 2.24
Mn(C <sub>5</sub> O <sub>5</sub> )(H <sub>2</sub> O) <sub>3</sub> <sup>(e), (f)</sup>	to C <sub>5</sub> O <sub>5</sub> : 2.172 (8), 2.253 (8) to H <sub>2</sub> O: 2.210 (8), 2.226 (9)
(Pyridoxylidenevaline)- manganese(II) <sup>(g)</sup>	2.08 (1), 2.17 (1)

(a) Onuma & Shibata (1970); Montgomery & Lingafelter (1968).  
(b) Osaki, Nakai & Watanabe (1964). (c) Koda, Ooi & Kuroya (1972). (d) Danielson & Rasmussen (1963). (e) C<sub>5</sub>O<sub>5</sub> = croconate.  
(f) Glick & Dahl (1965). (g) Willstader, Hamor & Hoard (1963).

ganese(II) (Montgomery & Lingafelter, 1968; Onuma & Shibata, 1970), diaquabis(formato)manganese(II) (Osaki, Nakai & Watanabe, 1964), and dimeric allylaminebis(2,4-pentanedionato)manganese(II) (Koda, Ooi & Kuroya, 1972) as well as the complex [Mn<sup>2+</sup>(POCl<sub>2</sub>)<sub>2</sub>(EtO<sub>2</sub>CMe)<sub>2</sub>] (Danielson & Rasmussen, 1963) all possess six-coordination of this type.

The Mn—O bond distances to the β-ketoenolate O atoms [2.088 (1) and 2.136 (1) Å] are in good agreement with those in similar complexes (Table 4). The coordinate Mn—O(H<sub>4</sub>furan) bond distance is not unexpectedly longer [2.285 (2) Å], and is marginally longer than the coordinate bond distances between Mn and the O atoms of water and ethyl acetate (Table 4).

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## Bis(1-tert-butyl-2,3-dimethylisourea)dichloropalladium(II)

BY F. W. B. EINSTEIN\* AND J. S. FIELD†

*Department of Chemistry, Simon Fraser University, Burnaby, BC V5A 1S6, Canada*

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**Abstract.** [Pd(C<sub>7</sub>H<sub>16</sub>N<sub>2</sub>O)<sub>2</sub>Cl<sub>2</sub>], C<sub>14</sub>H<sub>32</sub>Cl<sub>2</sub>N<sub>4</sub>O<sub>2</sub>Pd, monoclinic, C2/c, *a* = 12.947 (9), *b* = 17.362 (13), *c* = 10.194 (6) Å, β = 112.16 (2)°, *V* = 2122.0 Å<sup>3</sup>, *Z* = 4,

The (bppd) group chelates the Mn almost symmetrically, although the difference in the two Mn—O bond distances (0.048 Å) is substantially greater than the estimated standard deviations. The two endocyclic C—O [C(11)—O(2) and C(13)—O(1)] and C—C [C(11)—C(12) and C(12)—C(13)] bond distances are nearly equal, within experimental error, and have values which are intermediate between those for single and double bonds, indicating complete π-electron delocalization over the β-ketoenolate system.

Because of the crystallographic centrosymmetry of the molecule, the coordinated H<sub>4</sub>furan molecules, which occupy mutually *trans* positions, are exactly coplanar, as are the two equivalent β-ketoenolate-manganese heterocycles. The two phenyl rings are twisted with respect to the β-ketoenolate-manganese rings by 25.63 and 15.88°.

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*D*<sub>c</sub> = 1.46, *D*<sub>m</sub> = 1.45 Mg m<sup>-3</sup>, Mo Kα<sub>1</sub> radiation, λ = 0.70926 Å, μ(Mo Kα) = 1.12 mm<sup>-1</sup>, final *R* = 0.054 for 1510 observed reflections, *T* = 293 (1) K. The Pd atom has a *trans* square-planar environment, being coordinated to the Cl atoms (along a crystallographic twofold axis) and to the imine N atoms of the isourea ligands. Significant bond lengths are Pd—Cl =

\* Author to whom correspondence should be addressed.

† Present address: Department of Chemistry, University of the Witwatersrand, Jan Smuts Avenue, Johannesburg, South Africa.